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Comparative study on the photocatalytic decomposition of methanol on TiO₂ modified by N and promoted by metals

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ABSTRACT

The photo-induced vapor-phase reaction of methanol was investigated on Pt metals deposited on pure and N-doped TiO₂. Infrared spectroscopic measurements revealed that illumination of the CH₃OH–TiO₂ and CH₃OH–M/TiO₂ systems led to the conversion of adsorbed methoxy species into adsorbed formate. In the case of metal-promoted TiO₂ catalysts CO bonded to the metals was also detected. Pure titania exhibited very little photoactivity, its efficiency, however, increased with the narrowing of its bandgap by N-doping, a feature attributed to the prevention of electron–hole recombination. Deposition of Pt metals on pure and N-doped TiO₂ dramatically enhanced the extent of photoreaction of methanol even in visible light: hydrogen and methyl formate with selectivities of 83–90% were the major products. The most active metal was Pt followed by Pd, Ir, Rh, and Ru. The effect of metal was explained by a better separation of charge carriers induced by illumination and by enhanced electronic interaction between metal nanoparticles and TiO₂.

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1. Introduction

In the last two decades an extensive research was devoted to the generation of hydrogen by the thermal decomposition of oxygenated organic compounds [1–3]. Supported Pt metals were found to be the most active catalysts [4–7], although Mo₂C prepared by the reaction of MoO₃ with multiwall carbon and carbon Norit exhibited also high activity [8,9]. Taking into account the requirement of fuel cell, a growing attention is also paid to the production of hydrogen free of CO. For this purpose the thermal decomposition of formic acid on supported metals seemed to be the most appropriate reaction [10–14]. Further step in this area is to generate hydrogen by photocatalytic reactions at room temperature. Recently we examined the photolysis of ethanol [15] and formic acid [16] on TiO₂-based materials with the aim to select the most effective catalysts and work out more suitable experimental conditions. It was reported that in the presence of water hydrogen free of CO can be produced in the photolysis of formic acid on Rh/TiO₂ at room temperature [16].

In the continuation of our research program in this work we deal with the photocatalytic reaction of methanol. This alcohol is one of the perfect and ideal resources for the generation of hydrogen and other organic compounds. Its photodecomposition has been the subject of several studies [17–37]. Most of them were

performed in liquid phase. Mainly TiO₂ was used as a photocatalyst promoting by Cu, Pt, Pd, Au, and Ag. All these metals enhanced the extent of the decomposition of methanol in ultraviolet light. In the visible light only few experiments were executed [19,30,33]. An interesting feature of the thermal reaction of methanol is that besides the well known degradation into CO and H₂



by certain catalysts it is converted into methyl formate and H₂ [38–46,48,49]



Methyl formate has been considered as a precursor in the synthesis of formamide, dimethyl formamide, acetic acid, propionic acid, cyanhydric acid, and several other materials [45], therefore its efficient production represents technological importance. Methyl formate is mainly synthesized by the dehydrogenation of methanol over Cu-based catalyst at higher temperatures. However, recent works showed that it is also formed in the photo-oxidation of methanol at room temperature [31,34–37]. In the present study we examine the photodecomposition of methanol on pure and metal-promoted TiO₂. Attempts will be also made to convert methanol into other compounds in the visible light by narrowing the bandgap of TiO₂ by N-doping.

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2. Experimental

2.1. Materials

Two types of TiO₂ were used: Hombikat, UV 100 (300 m²/g), and Degussa, P 25 (50 m²/g). For the preparation of N-doped TiO₂ we applied the description of Beranek and Kisch [47], who reacted TiO₂ with urea and calcined the catalyst at different temperatures. This sample is noted with “SK”. N-modified TiO₂ sample (named “SX”) was also produced following the description of Xu et al. [48]. Titanium tetrachloride was used as a precursor. After several steps the NH₃-treated TiO₂ slurry was vacuum dried at 353 K for 12 h, followed by calcination at 723 K in flowing air for 3 h. Metal-promoted TiO₂ samples were prepared by impregnating pure or doped TiO₂ with the solution of metal compounds to yield a nominal 2 wt% metal. The following salts of Pt metals were used: H₂PtCl₆·6H₂O, Pd(NO₃)₂, RhCl₃·3H₂O, H₂IrCl₆, and RuCl₃·3H₂O. The suspension was dried at 373 K and annealed at 573 K for 1 h. For IR studies the dried samples were pressed in self-supporting wafers (30 × 10 mm ~10 mg/cm²). For photocatalytic measurements the sample (70–80 mg) was sprayed onto the outer side of the inner tube from aqueous suspension. The surface of the catalyst film was 168 cm². The catalysts were oxidized at 573 K and reduced at 573 K in the IR cell or in the catalytic reactor for 1 h. Methanol was the product of Scharlau with a purity of 99.98%.

2.2. Methods

For FTIR studies a mobile IR cell housed in a metal chamber was used. The sample can be heated and cooled at 150 K. The IR cell can be evacuated to 10^{−5} Torr using a turbo molecular pumping system. The samples were illuminated by the full arc of a Hg lamp (LPS-220, PTI) outside the IR sample compartment. The IR range of the light was filtered by a quartz tube (10 cm length) filled with triple distilled water applied at the exit of the lamp. The filtered light passed through a high-purity CaF₂ window into the cell. The light of the lamp was focused onto the sample. The output produced by this setting was 300 mW cm^{−2} at a focus of 35 cm. The maximum photon energy at the sample is ca. 5.4 eV. After illumination, the IR cell was moved to its regular position in the IR beam. Infrared spectra were recorded with a Biorad (Digilab, Div. FTS 155) instrument with wavenumber accuracy of ±4 cm^{−1}. All the spectra presented in this study are difference spectra.

For the determination of bandgap of solids, diffuse reflectance spectra of TiO₂ samples were obtained using an UV/Vis spectrophotometer (OCEAN OPTICS, Typ.USB 2000) equipped with a diffuse reflectance accessory. The surface area of the catalysts was determined by BET method with N₂ adsorption at ~100 K. The dispersion of metals was determined by the adsorption of H₂ at room temperature. Data are listed in Table 1.

Photocatalytic reaction was followed in the same way as described in our previous paper [15]. The photoreactor (volume: 970 ml) consists of two concentric Pyrex glass tubes fitted one into the other and a centrally positioned lamp. It is connected to a

gas-mixing unit serving for the adjustment of the composition of the gas or vapor mixtures to be photolyzed in situ. We used a 15 W germicide lamp (type GCL 307T5L/CELL, Lighttech Ltd., Hungary), which emits predominantly in the wavelength range of 250–440 nm, its maximum intensity is at 254 nm. For the visible photocatalytic experiments another type of lamp was used (Lighttech GCL 307T5L/GOLD) with 400–640 nm wavelength range and two maximum intensities at 453 and 545 nm. The approximate light intensities at the catalyst films are 3.9 mW/cm² for the germicide lamp and 2.1 mW/cm² for the other lamp. Methanol (~9.0%, 2160 μmol) was introduced in the reactor through an externally heated tube avoiding condensation. The carrier gas was Ar, which was bubbled through methanol at room temperature. The gas-mixture was circulated by a pump. The reaction products were analyzed with a HP 5890 gas chromatograph equipped with PORAPAK Q and PORAPAK S packed columns. The sampling loop of the GC was 500 μl. The amounts of all products were related to this loop.

3. Results

3.1. Characterization of the catalysts

In our previous paper we determined the bandgap energy of several TiO₂ + N catalysts [15] following the method described by Beranek and Kisch [47]. In the present work this characteristic was measured only for the new samples. The Kubelka–Munk function $F(R_{\infty})$ vs. wavelength curves were obtained from diffuse reflectance data, and the equation $\alpha = A(h\nu - E_g)^n/h\nu$ was used in the calculation, where α is the absorption coefficient, A is a constant, $h\nu$ is the energy of light and n is a constant depending on the nature of the electron transition. Assuming an indirect bandgap ($n = 2$) for TiO₂, with α proportional to $F(R_{\infty})$, the bandgap energy can be obtained from the plots of $[F(R_{\infty})h\nu]^{1/2}$ vs. $h\nu$, as the intercept at $[F(R_{\infty})h\nu]^{1/2} = 0$ of the extrapolated linear part of the plot. The values obtained for pure and doped TiO₂ are collected in Table 1. This shows that depending on the preparation the incorporation of N into TiO₂ considerably lowers its bandgap. In contrast, no or only slight decrease occurred by doping TiO₂ with fluorine.

3.2. FTIR study of photolysis of methanol

The primary aim of the IR study is to ascertain the development of adsorbed complexes on the effect of illumination on TiO₂, and to establish the influence of metal deposition on these features. As observed before [41] prior to the addition of methanol the IR spectrum of TiO₂ showed the usual ν_{OH} absorption at 3720, 3671, and 3648 cm^{−1}. The adsorption of methanol resulted in a very broad absorption region between 3500 and 2700 cm^{−1} due to the high concentration of OH groups. In the C–H stretching region absorption bands of different intensities were traced at 2948, 2935–2938, 2923, 2914, 2891, 2873, 2844, 2842, and ~2810 cm^{−1} (not shown). In the low frequency range weak bands appeared at 1561, 1445, 1442, 1380, 1361, 1157, and ~1080 cm^{−1} (Fig. 1A). Illumination of the CH₃OH vapor–TiO₂ system caused no observable change in the high frequency range, but led to the significant intensification of the bands in the low frequency region (Fig. 1A). We experienced similar changes on the IR spectra of metal/TiO₂ samples (Fig. 1B and C). A new feature was the sudden appearance of a strong band between 2000 and 2045 cm^{−1} due to adsorbed CO, which grew only slightly with the progress of illumination. This is illustrated in Fig. 1D.

When adsorbed methanol was irradiated the first change was the instant appearance of the CO band at 2000–2045 cm^{−1}, which became larger as a result of continuous illumination (not shown).

Table 1
Some characteristic data for pure and doped TiO₂.

Sample	Pretreatment temperature (K)	Surface area (m ² /g)	Bandgap (eV)
TiO ₂ 3.17, 3.21	(Hombikat)	As received	~300
TiO ₂ + N (SK)	450	260	3.04
TiO ₂ + N (SK)	573	115	3.00
TiO ₂ + N (SK)	773	81	2.17
TiO ₂ (SX)	723	265	3.02
TiO ₂ + N (SX)	723	79	~1.96

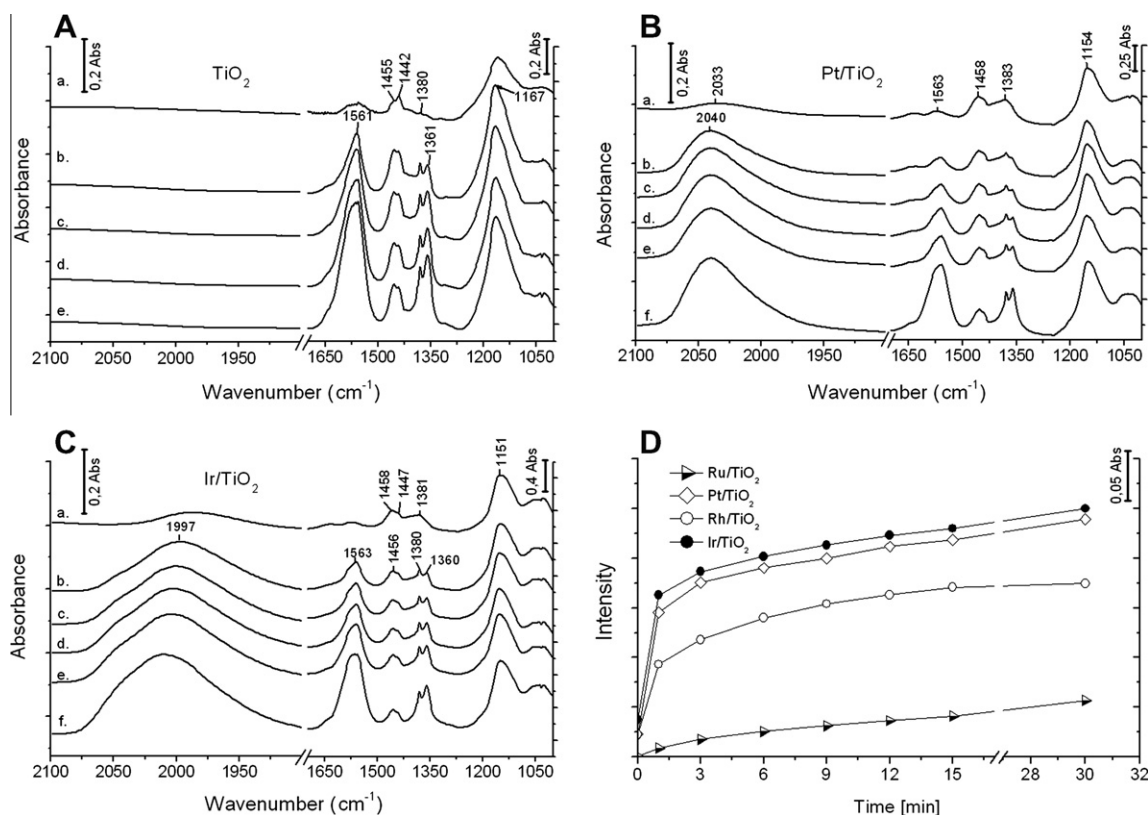


Fig. 1. Effects of illumination time on the FTIR spectra of TiO₂ (A), Pt/TiO₂ (B), and Ir/TiO₂ (C) obtained in the presence of CH₃OH vapor and on the intensity of CO band at 2000–2060 cm^{−1} (D). a. 0 min, b. 1 min, c. 3 min, d. 6 min, e. 9 min, f. 30 min.

In the high frequency range a pair of strong absorption bands at 2936–2939 and 2835–2839 cm^{−1} of almost same intensity became the dominant spectral features for all M/TiO₂ catalysts. With the increase of illumination time both bands slowly attenuated. In the low frequency range absorption bands appeared at ~1558–1578, ~1458, ~1442, 1359–1380, 1158–1164, and 1026–1030 cm^{−1}. The intensity of the absorption bands at 1558–1578 cm^{−1} increased, while the other ones slightly attenuated with the time of irradiation. In Fig. 2 spectra of 2750–3000 and 1100–1650 cm^{−1} regions are shown for three M/TiO₂ catalysts. IR bands observed and their possible assignment are presented in Table 2.

3.3. Photocatalytic decomposition of methanol on pure and N-doped TiO₂

Illumination initiated the decomposition of methanol on TiO₂ at 300 K, but the conversion was very low: ~1.5% in 210 min (Fig. 3A). The main products are methyl formate and H₂ with very small amounts of CO and CO₂. The selectivity of the formation of methyl formate is very high, ~90%. The photoactivity of TiO₂ was significantly enhanced by N doping, and the promoting effect of N increased with the modification temperature of TiO₂ + N sample. This feature is more pronounced when the amount of methyl formate formed is related to the surface area of the TiO₂ samples (Fig. 3B). When the photolysis was performed in the visible light, the extent of photodecomposition markedly decreased, but the effect of N-doping was appreciable.

It was a general observation that the amount of H₂ formed was much less than that of methyl formate. We experienced a similar lack in H₂ in the photodecomposition of ethanol and formic acid on TiO₂ [15,16]. We assume that hydrogen may reduce the TiO₂

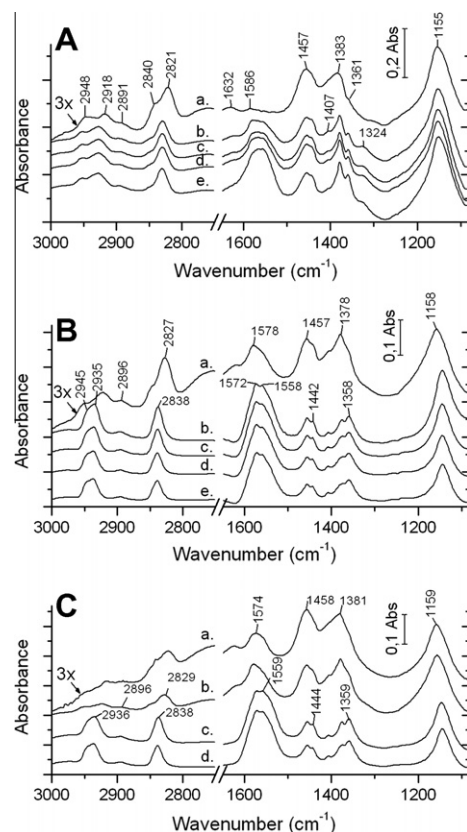


Fig. 2. Effects of illumination time on the FTIR spectra of adsorbed CH₃OH on Rh/TiO₂ (A), Pt/TiO₂ (B), Ir/TiO₂ (C) 300 K. a. 0 min, b. 1 min, c. 3 min, d. 9 min, e. 30 min.

Table 2

IR vibrational frequencies of methoxy species on TiO₂ and those observed following the illumination of adsorbed methanol on M/TiO₂ catalysts at 300 K.

Vibrational mode	TiO ₂ [40]	Ru/TiO ₂ [present work]	Pd/TiO ₂ [present work]
$\nu_{as}(\text{CH}_3)$	(2965)		
$\nu_s(\text{CH}_3)$	2930	2933	2939
$2\delta_s(\text{CH}_3)$	2830	2835	2839
$\delta_{as}(\text{CH}_3)$	1462	1457	1456
$\delta_s(\text{CH}_3)$	1436	1442	1443
$\nu(\text{CO})$	1151	1158	1114
$\nu(\text{CO})$	1125	1029	1023

surface or combine with surface oxygen to yield OH groups. In the case of N-doped TiO₂ a fraction of H₂ can also react with the surface species produced by the preparation of TiO₂ + N samples [15].

3.4. Effects of Pt metals

In the next experiments, we examined the effects of the deposition of various Pt metals on TiO₂. All metals exerted a dramatic influence on the photodecomposition of methanol. The conversion attained a value of 30–70% in 210 min. In Fig. 4 the results obtained on various M/TiO₂ catalysts are displayed. On the basis of these data, the activity order is Pt, Pd, Ir, Rh, and Ru. The major product is H₂ followed by methyl formate (C₂H₄O₂). Much less formaldehyde, CO, CO₂, and CH₄ were evolved. The formation of minor products obtained over 2% Pd/TiO₂ is shown in Fig. 5A. The selectivity of methyl formate was very great on all catalysts. Highest values were measured at the beginning of the reaction (87–97%), which lowered to 83–90% at the termination of the experiments, at 210 min. The CO/H₂ ratio was very low, 0.01–0.02 (Table 3). In order to judge the importance of TiO₂ support and that of metal/TiO₂ contact, the photolysis of methanol was also carried out on 2% Pd/SiO₂ catalyst. As can be seen in Fig. 5B, we measured only very slight decomposition; the conversion approached 1% in 210 min. When metals were deposited on N-doped TiO₂ an appreciable enhancement was observed in the photoactivity of the catalysts.

This is illustrated by the results obtained on Rh/TiO₂ (SX sample) in Fig. 6.

Although the catalyst sample was cooled during the photolysis, the possibility cannot be excluded that the illumination caused a temperature rise of the catalyst. However we measured not more than 1–2° increase in the sample temperature as a result of irradiation. We also examined the thermal reaction on the Pt/TiO₂ and Pd/TiO₂ layer used for photolysis without illumination. No decomposition was observed on either catalyst at 300–423 K in 60 min. The decomposition started at 473 K, it reached ~1–2% in 60 min. The results of these control experiments lead us to exclude the contribution of thermal effects to the decomposition of methanol induced by photolysis. An interesting feature of these experiments is that only very small amounts of methyl formate, less than 5–8% was formed in the thermal decomposition at higher temperature, 523 K, when the conversion of methanol reached 5–10%.

Detailed experiments were performed in the visible light using a lamp emitting at 400–640 nm. Whereas the photoactivity of pure TiO₂ is hardly detectable in this wavelength range, the reaction was well measurable on TiO₂ doped with N. This was observed both for SK and SX samples. The positive influence of N-doping was more appreciable in the case of metal-promoted TiO₂ samples. Fig. 7 depicts the photocatalytic effects of Rh, Ir, and Pd deposited on pure and N-modified TiO₂ (SX). The comparison of the data immediately reveals that the photoactivity of the N-modified catalysts is markedly higher than that of M/TiO₂ free of nitrogen. This is reflected in the conversion of methanol and in the amounts of the products formed. In the case of Ir/TiO₂ the incorporation of N into TiO₂ increased the amount of hydrogen by a factor of 10.

4. Discussion

4.1. IR studies

FTIR study of the adsorption of methanol on titania has been the subject of extensive research [23,34,40,41]. Based on the results of previous studies the bands registered at 2948 and 2844 cm⁻¹ can be assigned to the asymmetric and symmetric CH₃ stretching frequencies of adsorbed CH₃OH, and those at 2933–2939 and 2835–2839 cm⁻¹ to adsorbed CH₃O. The spectral features in

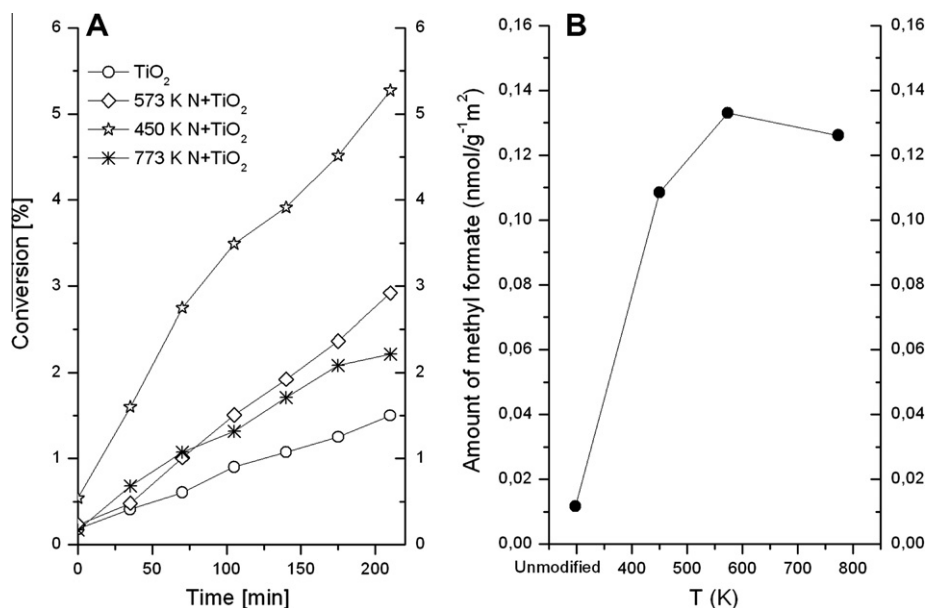


Fig. 3. Effects of the modification temperature of N-doping of TiO₂ (SK) on the conversion of CH₃OH (A) and on the formation of methyl formate (B) related to the surface area of the TiO₂ samples.

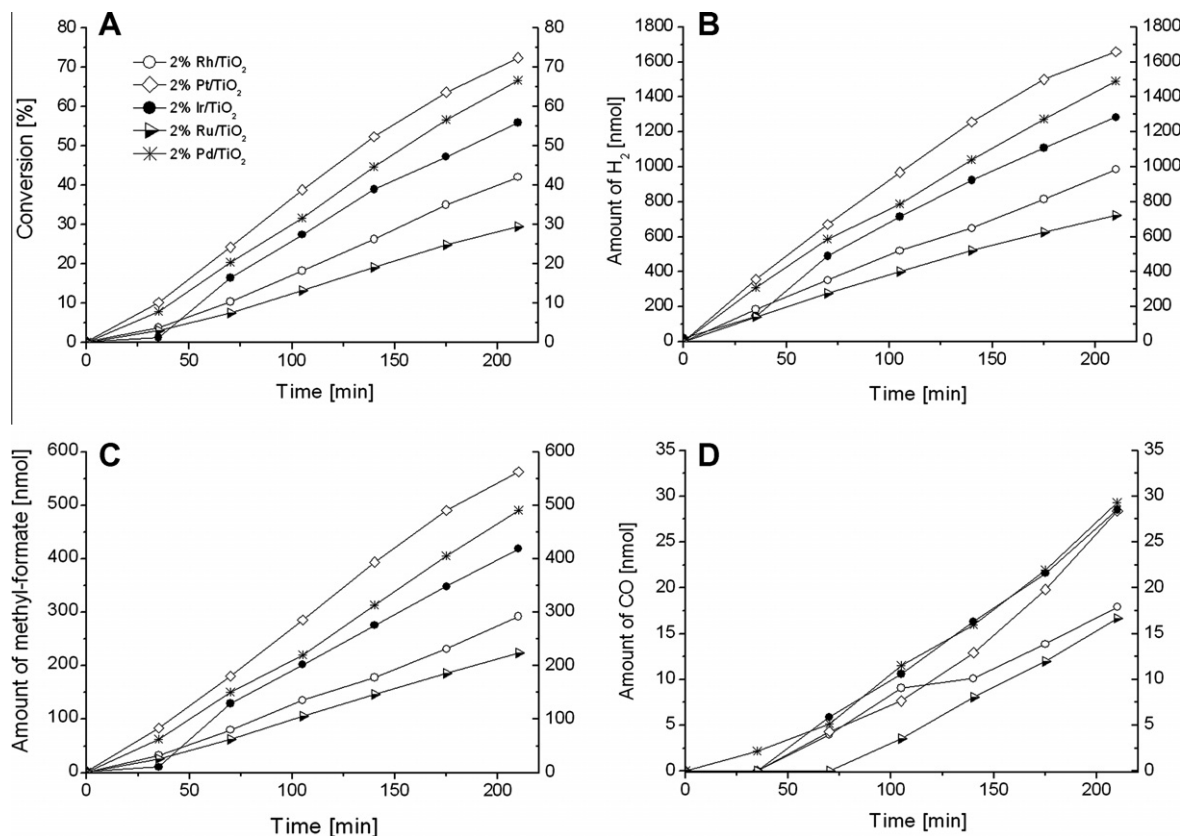


Fig. 4. Comparison of photocatalytic effects of Pt metals deposited on TiO₂ (Hombikat). Conversion of CH₃OH (A), formation of H₂ (B), methyl formate (C), and CO (D).

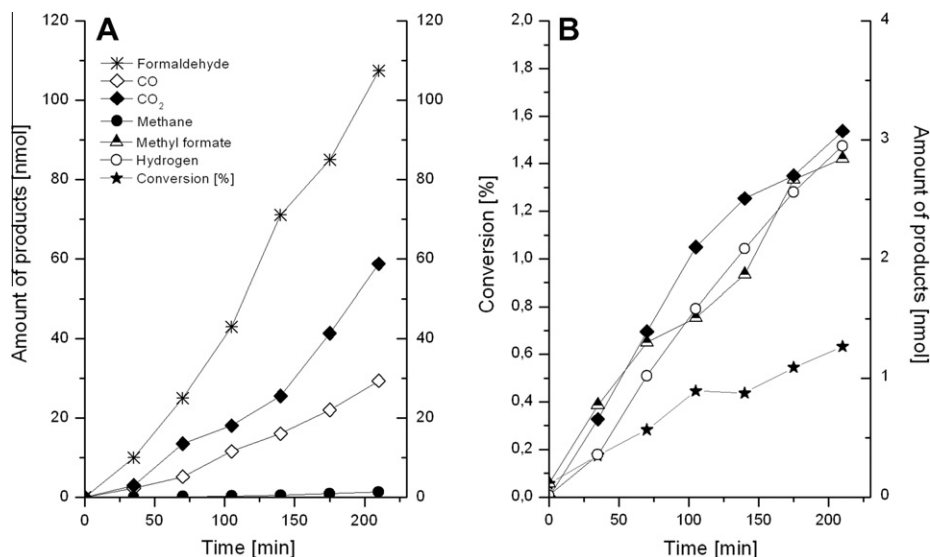


Fig. 5. Minor products of the photodecomposition of CH₃OH on 2% Pd/TiO₂ as a function of illumination time (A) and the photocatalytic effect of Pd/SiO₂ (B).

1000–1200 cm⁻¹ range are due to C–O stretching of the two adsorbed species (Table 2). Accordingly we can count them with the occurrence of the following steps

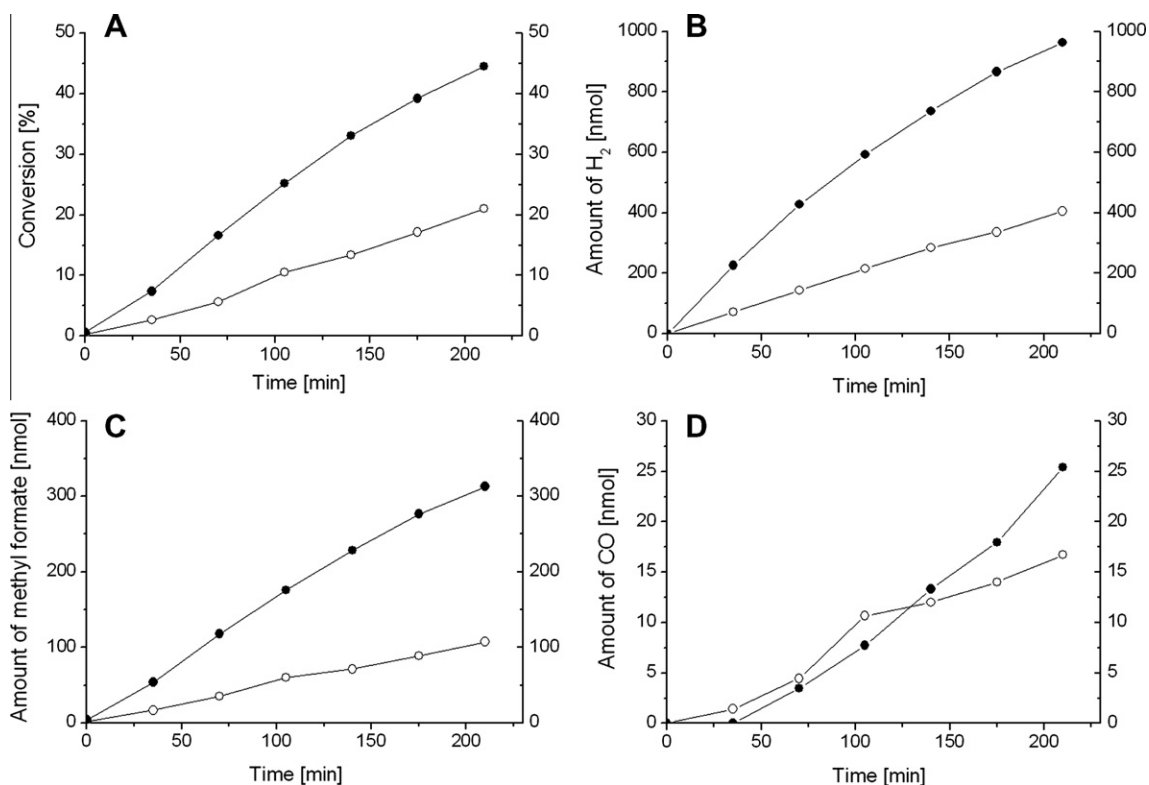


The fact that after photolysis of methanol adsorbed on metal/TiO₂ samples two absorption features at 2936–2939 and 2835–2839 cm⁻¹ dominated the spectra suggests that the illumination

made the dissociation process almost complete. In addition, a new absorption band also appeared at 1558–1578 cm⁻¹, which is the most characteristic vibration of the formate species [16,40,41]. The development of these spectral features is more expressed in the case of M/TiO₂ samples (Fig. 2). Taking into account the results of photocatalytic measurements adsorbed formate very likely formed in the dissociation of methyl formate produced by the photo-conversion of methanol, as the IR spectrum of methyl formate does not contain vibrations at ~1558–1578 cm⁻¹ similar to molecularly adsorbed formic acid [40]. The appearance of

Table 3Characteristic data for M/TiO₂ catalysts and for photoreaction of methanol on M/TiO₂.^a

Samples	Dispersion of metals (%)	Work function of metal (eV)	Conversion (%)	<i>N</i> _{M-formate}	M-formate selectivity (%)	CO/H ₂ ratio	Yield M-formate
Pt/TiO ₂	13	5.70	71.4	0.713	87.1	~0.017	62.2
Rh/TiO ₂	16	4.98	38.7	0.145	88.4	~0.018	34.2
Ir/TiO ₂	54	5.76	55.1	0.120	88.4	~0.022	48.7
Pd/TiO ₂	26	5.12	67.1	0.153	83.1	~0.019	55.8
Ru/TiO ₂	6	4.71	28.8	0.296	90.4	~0.023	26.0

*N*_{M-formate} = the amount of methyl formate formed in 105 min related to the number of surface metal atoms.^a Data for photocatalysis were obtained in 210 min of reaction.**Fig. 6.** Effects of N-doping of TiO₂ (SX) on the photocatalytic decomposition of CH₃OH on 2% Rh/TiO₂. Conversion of CH₃OH (A), formation of H₂ (B), methyl formate (C), and CO (D). ○ 2% Rh/TiO₂, ● 2% Rh/TiO₂ + N.

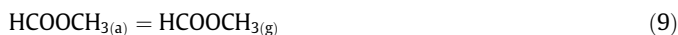
vibration bands at 2000–2060 cm⁻¹ following the adsorption of methanol on M/TiO₂ samples at 300 K suggests that a fraction of adsorbed methoxy group underwent a complete dissociation on all M/TiO₂ samples.



Illumination promoted this dissociation process as indicated by the strengthening of the CO bands. It is to be noted that in the most cases only the linearly bonded CO was formed and there was no spectral indication of the presence of dicarbonyl (M(CO)₂) species due to the oxidative disruption of metal crystallites [50].

4.2. Photocatalysis

Photocatalysis is in harmony with the results of IR studies illumination induced the conversion of methanol into methyl formate. This can be described by the following elementary steps



It is generally accepted that the slow, rate determining step in the decomposition of methanol is the cleavage of one of the C–H bonds in the adsorbed CH₃O species. The occurrence of this step on TiO₂ at 300 K, however, requires activation, as otherwise no reactions occur at all. As illumination initiated the reaction of methanol on TiO₂ at 300 K, we assume that this is the result of a donation of photoelectrons formed in the photo-excitation process



to the methoxy species:



This leads to the activation and decomposition of methoxy complex according to the Eq. (6). Product analysis shows that instead of complete decomposition to H₂ and CO, the major process is the recombination of CH₂O or its reaction with the methoxy group

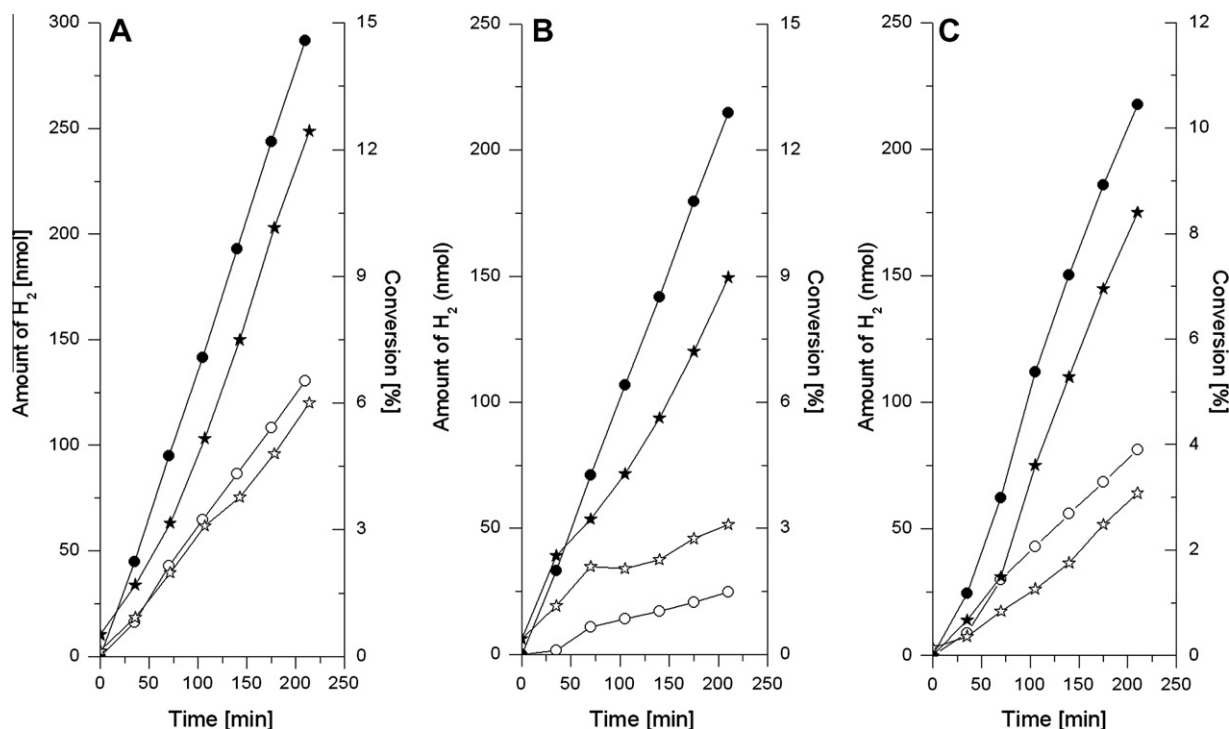
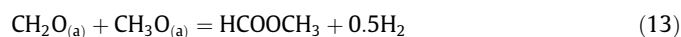


Fig. 7. Effects of N-doping of TiO₂ (SX) on the photocatalytic decomposition of CH₃OH in the visible light on 2% Rh/TiO₂ (A), 2% Ir/TiO₂ (B), and 2% Pd/TiO₂ (C). ○ TiO₂, ● ★ TiO₂ + N, ★ conversion, ○ ● H₂ formation.



to give methyl formate (Eqs. (8) and (13)). However, even the photo-induced reaction occurred to only a very limited extent on pure TiO₂: the conversion of the decomposition of methanol was less than ~2% in 210 min. It means that the recombination of electron and hole occurs more quickly. The incorporation of N into TiO₂, however, appreciably increased the extent of photodecomposition (Fig. 3A and B). In view of the change in the bandgap of N-doped TiO₂ with the modification temperature (Table 1), it may be concluded that the extent of photolysis of methanol on TiO₂ is enhanced by the narrowing of the bandgap of TiO₂. This can be attributed to the prevention of electron–hole recombination.

A dramatic enhancement in the photolysis of methanol occurred, when Pt metals were deposited onto TiO₂. The positive influence of the narrowing of the bandgap of TiO₂ appeared in the performance of metal-promoted TiO₂ samples both in UV and visible light (Figs. 6 and 7). In the explanation of the effects of metals several factors should be considered. First the dissociative adsorption of methanol also proceeds on Pt metals, and the methoxy species formed is much more reactive compared to that located on TiO₂. In spite of the lower stability, the dominant reaction pathway of methoxy species is still the formation of methyl formate described before (Eqs. (8) and (13)). The simple decomposition to hydrogen and CO (Eq. (1)) occurring in the thermal reaction on supported metals is a negligible process, as CO is formed only in minor amounts. It is important to emphasize that we measured no or very slight thermal reaction of methanol below 473 K even on the most active Pt/TiO₂ film. Taking into account all these findings we assume that the occurrence of the photoreaction on M/TiO₂ catalysts is due to the enhanced formation and decomposition of activated CH₃O at the metal/TiO₂ interface.

The promoting effect of metal deposition on TiO₂ has been observed in a number of photoreactions [51]. This effect was explained by a better separation of charge carriers induced by

illumination and by improved electronic communication between metal particles and TiO₂. We believe that the electronic interaction between the metal and n-type TiO₂ also plays an important role in the enhanced photoactivity of M/TiO₂. As the work function of TiO₂ (~4.6 eV) is less than that of Pt metals (4.98–5.7 eV), electron transfer occurs from TiO₂ to metals, which increases the activation of adsorbed molecules. The role of such electronic interaction in the activity of a TiO₂-supported metals was first established in the case of the decomposition of formic acid on Ni/TiO₂, when (as far as we are aware) TiO₂ was first used as a support [52,53]. Variation of the electron density or the work function of TiO₂ doping with altrivalent cations influenced the activation energy of the decomposition of formic acid. We assume that the illumination enhances the extent of electron transfer from TiO₂ to metals at the interface of the two solids, leading to increased decomposition.

An interesting finding of this study is that the photolysis of CH₃OH–M/TiO₂ system at 300 K produces a significant amount of methyl formate with high selectivities and yields, which does not occur in the thermal decomposition of methanol on metal-promoted TiO₂ catalysts even at higher temperature. This means that couplings of formaldehyde (Eqs. (8) and (13)) into methyl formate are faster than its complete decomposition (Eq. (7)).

5. Conclusions

- IR spectroscopic studies revealed that illumination of CH₃OH–TiO₂ system induced the formation of adsorbed formate species.
- The photodecomposition of methanol on pure TiO₂ occurred only to a limited extent. The main process is the production of methyl formate. Doping TiO₂ with N increased its photoactivity.
- Deposition of Pt metals on pure and N-doped TiO₂ dramatically enhanced the photoreaction of methanol into methyl formate, which formed with a selectivity of 85–90%.

- (iv) Lowering the bandgap of TiO₂ through N incorporation facilitated the photolysis of methanol on TiO₂ and M/TiO₂ even in visible light.

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